

1.110.930



PATENT SPECIFICATION

DRAWINGS ATTACHED

1.110.930

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COMPLETE SPECIFICATION

Polymeric Composition and process of preparation

We, MONSANTO COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 800, North Lindbergh Boulevard, St. Louis 66, State of Missouri, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polymeric compositions containing an inorganic filler. The invention further relates to a process for preparing the compositions.

It has been proposed to increase the modulus (stiffness) of a polymer by addition of a rigid filler. Tensile and flexural strength can also be increased by inclusion of a thoroughly dispersed rigid filler if good adhesion between polymer and filler can be achieved. Resistance to impact, however, is reduced by addition of a rigid filler and decreases dramatically as the volume fraction of filler increases. Diminution of impact strength occurs in all prior art compositions regardless of good dispersion and wetting. Theoretical considerations, which must take into account stress concentrations around rigid inclusions in a plastic matrix, confirm these empirical observations. Expressed in simple terms, a mixture of a plastic and a rigid phase will produce a composite of increased rigidity simply because some of the energy required to stretch or bend the composite is expended on the rigid phase. Application of a uniaxial stress to a composition containing a rigid sphere in a less rigid matrix results in a stress concentration in the matrix at the surface of the sphere of as much as three times the stress at some point a large distance from the spherical surface. If the rigid inclusion is in the shape of a rod, whisker, flake, needle or granule with sharp corners, the stress con-

centration at some portions of the filler surface will be even greater. When a filled polymer is subjected to sudden high-energy loading, the stress concentrations at filler surfaces provide sites for failure, which should occur at stress levels below that necessary to cause failure in an unfilled system. The conclusion that the modulus increases while the impact strength diminishes at increasing levels of rigid filler loading in a polymer is supported both by mathematical theory and empirical data.

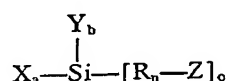
Combination of increased tensile and impact strengths in polymeric compositions has been obtained by incorporation of fibrous materials such as glass fibres into polymeric matrices. Use of fibrous reinforcement has the disadvantage, however, of requiring more difficult, time-consuming processing steps plus higher costs for the fibres. Further, fibre reinforced compositions can only be readily fabricated into finished articles by moulding the compositions into a finished shape simultaneously with incorporation of the fibre into the polymer. Use of a filler with a low length to diameter ratio (l/d) permits production of a relatively low cost composition which can be compounded in one location and shipped to another for final fabrication. As yet, it has not been possible to combine versatility attendant to the use of fillers in polymeric compositions with the superior properties achieved by the use of fibrous reinforcement.

A new polymeric composition has now been discovered with improved properties in this respect.

The present invention is directed to polymeric compositions comprising a polyolefin as herein defined, from 10 to 60% by volume based on the total composition of an inorganic filler having an average surface area of from 0.5 to 10 square meters per gram

[Price

and an l/d ratio of 10 to 1 or less, and an organosilane of the formula



I.

where X is a hydrolysable group capable of reacting with a hydroxyl group, Y is a monovalent hydrocarbon group, R is an alkylene group having from 1 to 20 carbon atoms, Z is a group capable of reacting with a free radical, n is 0 or 1, a is 1, 2 or 3, b is 0, 1 or 2, c is 1, 2 or 3 and the sum of a+b+c equals 4. Preferably the compositions are characterised by an Izod notched impact strength at least 10% greater than the impact strength of the unfilled polyolefin and by a yield strength and tensile strength at least undiminished by comparison to the corresponding strengths of the unfilled polyolefin.

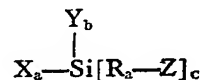
Polyolefins useful herein are those polymers (including copolymers and blends, both as defined below) formed from the polymerisation (which term includes copolymerisation) of α -olefins having up to 3 carbon atoms, i.e. ethylene or propylene. Preferred are those thermoplastic, substantially uncrosslinked polyethylenes and polypropylenes which have a tensile modulus of at least 1000 pounds per square inch. The term *substantially uncrosslinked* is used to refer to those polymers which are at least 70%, and preferably at least 90%, soluble in xylene at 110° C. This degree of solubility corresponds approximately to no more than about one crosslink per ten polymer molecules, and preferably considerably less. Suitable polymers include polyethylenes having densities at least 0.92 grams per cubic centimetre. Also included are the isotactic forms of polypropylene. Olefin copolymers can also be advantageously modified within the scope of the present invention. Copolymers usable herein are limited to those containing at least 50% by weight polymerised olefin and preferably at least 75% by weight polymerised olefin. Examples of monomers copolymerisable with an olefin include other olefins as isobutylene or butene-1, ethyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride, maleic anhydride and fumaric acid. Polyblends containing at least 50% by weight polymerised olefin are also included herein. The blends can be either mechanical or polymerisation blends and can be two- or multicomponent blends of a polyolefin or olefin copolymer with any other compatible polymer. Preferably the blends are mechanical polyblends containing at least 75% polyolefin and the balance an olefin copolymer. Examples of polymers which can be blended with polyethylene include ethylene/vinyl acetate, ethylene/vinyl chloride, ethylene/maleic anhydride, ethylene/ethyl acrylate,

ethyl acrylate, polymethyl methacrylate, polystyrene, and polyvinylidene chloride.

The fillers incorporated into the polymeric having a low surface area in the range of 0.5 to 10 square meters per gram. Excluded by the above limitation are the hydrated silicas and silicates and the plate-like inorganics such as kaolin, talc and mica. Preferred from the standpoint of economy plus performance are inorganic fillers having surface areas up to 3 square meters per gram. Considering only performance, fillers having surface areas above 4 or 5 square meters per gram are particularly preferred. As indicated above, the shape of the filler is an important consideration. Generally, fillers useful herein should have a length to diameter ratio (l/d) no greater than 10 to 1. Preferably, the overall size and shape of the particles should be such that they are capable of passing through a 325 mesh screen of the U.S. Sieve Series. More preferably, the fillers should have an average particle size in the range of 0.5 to 20 microns although particles as small as 100 to 200 millimicrons can also be used.

As previously stated, it is necessary that the filler be used in quantities ranging from 10 to 60%, preferably from 20 to 40% by volume of the total composition. Assuming a filler density of 2.7 and a polymer density of 0.96, the above ranges correspond to about 25 to about 90%, preferably from about 40 to about 65%, by weight filler based on the total composition. Examples of suitable fillers are inorganic siliceous minerals such as quartz, wollastonite, mullite, kyanite, chrysotile, cristobalite, crocidolite, fibrous aluminum silicate having the formula Al_2SiO_5 , spodumene and garnet. Additional fillers include inorganic nonsiliceous fillers such as alumina and hercynite, metals such as aluminum, tin, lead, magnesium, calcium, strontium, barium, titanium, zirconium, vanadium, chromium, manganese, iron, cobalt, nickel, copper and zinc, metal oxides such as oxides of the foregoing metals and metal salts such as heavy metal phosphates, sulfides and sulfates. Preferred fillers are those mentioned above which are further characterised by a somewhat refractory nature with a melting point above about 800° C, a Mohs Hardness of at least 4 and a water solubility of less than 0.1 gram per litre.

The organosilane in the composite formulation has functional groups capable of rendering it adherent to the filler surface and to the polymer surface. A formula for silanes having the above characteristics is as follows:



I.

where X is a hydrolysable functional group

capable of reaction with a hydroxyl group, Y is a monovalent hydrocarbon group, R is an alkylene group having from 1 to 20 carbon atoms, Z is a functional group capable of reaction with a free radical, n is 0 or 1, a is 1, 2 or 3, b is 0, 1 or 2, c is 1, 2 or 3 and the sum of $a+b+c$ equals 4.

Examples of functional groups attached to silicon atoms which will form adherent bonds to inorganic surfaces include hydroxy groups and alkoxy, cycloalkoxy, aryloxy, alkyl carboxylate, aryl carboxylate, alkoxycarbonyl, aryloxycarbonyl and halogen groups wherein the carbon-containing groups usually have eight or less carbon atoms.

In addition to inorganic-reactive groups on the coupler, there is also at least one functional group capable of forming adherent bonds to polyethylene under certain conditions. This condition is satisfied by including on the coupler a functional group capable of reacting with free radicals. Examples include

vinyl, allyl and other ethylenically unsaturated hydrocarbon groups, acryloxy and methacryloxy groups, amino, epoxy, isocyanato and cyano groups. To increase the stability of the functional silane, the free radical-reactive group is often attached to the silicon atom through an intermediate alkylene chain such as a propylene or cyclohexylene group. Generally, the intermediate chain, if present, can have from 1 to 20 carbon atoms.

Optionally, the silane can also contain one or two monovalent hydrocarbon groups which are chemically reactive with neither the inorganic nor the polymer. Their function can be to disperse the inorganic filler more efficiently in the polymer matrix or merely to alter the reactivity of the coupler with the inorganic filler or polymer. Examples of such groups include methyl, cyclohexyl and octadecyl groups. Examples of suggested silane couplers include

vinyl triethoxysilane, $\text{CH}_2 = \text{CHSi}(\text{OC}_2\text{H}_5)_3$;

vinyl methylchlorosilane,
 $\text{CH}_2 = \text{CHSi}(\text{CH}_3)\text{Cl}_2$;

methyl β -(methyldifluorosilyl) acrylate
 $(\text{F})_2(\text{CH}_3)\text{SiCH}=\text{CHCOOCH}_3$;

2-trimethoxysilylethyl methacrylate,
 $(\text{CH}_3\text{O})_3\text{SiC}_2\text{H}_4\text{OOC}(\text{CH}_3)=\text{CH}_2$;

3-triethoxysilylpropyl methacrylate,
 $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_3\text{H}_6\text{OOC}(\text{CH}_3)=\text{CH}_2$;

4-trichlorosilylbutyl acrylate,
 $(\text{Cl})_3\text{SiC}_4\text{H}_8\text{OOCCH}=\text{CH}_2$;

6-tricyclohexyloxysilylhexyl methacrylate,
 $(\text{C}_6\text{H}_{11}\text{O})_3\text{SiC}_6\text{H}_{12}\text{OOC}(\text{CH}_3)=\text{CH}_2$;

11-trimethoxy silylundecyl methacrylate,
 $(\text{CH}_3\text{O})_3\text{SiC}_{11}\text{H}_{22}\text{OOC}-\text{C}(\text{CH}_3)=\text{CH}_2$

18-triethoxysilyloctadecylacrylate,
 $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_{18}\text{H}_{36}\text{OOCCH}=\text{CH}_2$;

18-triacetoxysilyloctadecyl acrylate,
 $(\text{CH}_3\text{COO})_3\text{SiC}_{18}\text{H}_{36}\text{OOCCH}=\text{CH}_2$;

p-[3-trimethoxysilylpropyl] styrene,
 $(\text{CH}_3\text{O})_3\text{SiC}_3\text{H}_6\text{C}_6\text{H}_4\text{CH}=\text{CH}_2$;

β -[6-trichlorosilylhexyl] acrylonitrile,
 $(\text{Cl})_3\text{SiC}_6\text{H}_{12}\text{CH}=\text{CHCN}$;

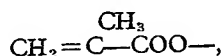
3-triethoxysilylpropylamine,
 $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_3\text{H}_6\text{NH}_2$;

3-trimethoxysilylpropyl nitrile,
 $(\text{CH}_3\text{O})_3\text{SiC}_3\text{H}_6\text{CN}$;

2-trichlorosilylethyl isocyanate,
 $\text{Cl}_3\text{SiC}_2\text{H}_4\text{NCO}$; and

gamma-glycidoxypropyltrimethoxysilane,
 $\text{CH}_2\text{CHCH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$.

Particularly preferred are coupling agents of formula I where the integer a is 3, b is 0, c is 1, n is 1, X is a chloro or alkoxy group having up to 4 carbon atoms, Z is a group containing ethylenic unsaturation, for example a methacryloxy group, i.e.



and R is an alkylene group having from 3 to 18 carbon atoms.

Organosilanes not inherently capable of reacting with free radicals can be pretreated or treated in situ with chemical compounds which can render the silane free radical-reactive. The same is true of silanes which have some degree of reactivity with free radicals—they also can be modified to improve their coupling activity. For example, an amino group on a silane coupler can be reacted with an unsaturated organic acid to provide a coupler having an ethylenic group instead of an amino group available for reaction with a free radical.

The amount of coupler with which the inorganic filler is treated is relatively small. As little as one gram of coupling agent per 1000 grams of filler produces a polymeric composition with mechanical properties superior to those of a polymeric composition containing an untreated filler. Generally, quantities of coupler in the range of 1 to 20 grams per thousand grams of filler have been found most satisfactory, although quantities in excess of that range can also be used. The quantity of coupler required for optimum mechanical properties in the filler-polyolefin composite varies depending upon the surface area of the inorganic filler and upon the particular chemical composition of the coupler. Experimentation indicates that quantities of coupler in excess of the amount necessary to provide a monomolecular layer over the inorganic filler particles usually have no beneficial effect on mechanical properties of the composite and may often result in some diminution of properties. As a result, quantities of coupler not exceeding the amount theoretically necessary to provide a monomolecular layer on the inorganic filler are usually used. The Examples set forth below provide specific treatments of inorganic fillers with couplers

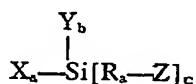
which have provided the reported degrees of success.

The coupler can be attached to the inorganic filler surface in several different ways. For instance, the two components can be joined by combining them in the presence of a solvent or dispersant for the coupler such as water, alcohol, dioxane, benzene, etc. Alternatively, the coupler can be dry blended with the inorganic filler. In either instance, the application of heat up to 200° C facilitates the complete reaction of coupler and inorganic filler. If the coupler is applied to the inorganic filler in the presence of a solvent, the heat to accelerate the coupler-filler reaction can be applied simultaneously with the removal of solvent by evaporation. A third related technique comprises adding coupler, inorganic filler and polymer together and mixing for a time sufficient to achieve coupler-filler combination.

Compositions of the present invention preferably have an Izod notched impact strength at least 10% greater than the impact strength of the unfilled polyolefin and a yield strength and tensile strength at least undiminished by comparison to the corresponding strengths of the unfilled polyolefin. Preferred are those compositions where both the yield strength and tensile strength are also improved by at least 10% over the unfilled polymer. Particularly preferred compositions are those where one or more of the abovementioned tensile or impact properties are improved by 20% or more. Employing some of the optimum processing conditions described below, it is possible to prepare composites having an impact strength at least double the impact strength of the unfilled polymer while at the same time having a tensile strength to yield and to break greater than that of the unfilled polymer. The yield point in a tensile test is that point on the stress-strain curve at which an increase in strain occurs without an increase in stress. The stress required to reach the yield point is the tensile strength to yield or simply the yield strength. The breaking point is that point on the stress-strain curve at which the specimen ruptures. The stress required to reach the breaking point is the tensile strength to break or simply the tensile strength. Tensile strengths and yield strengths are expressed in pounds per square inch and

are measured according to ASTM D—638 at a cross-head speed of 5 inches per minute. Impact strengths are expressed in foot-pounds per inch of notch and are measured according to ASTM D—256 Procedure A.

- 5 The filled polyolefins of the present invention are prepared by a) combining a polyolefin as herein defined and from 10 to 60% by volume inorganic filler having an average surface area of from 0.5 to 10 square meters per gram and an l/d ratio of 10 to 1 or less, said filler having adherently bonded to its surface an organosilane of the formula



- 15 where X is a hydrolysable group capable of reacting with an hydroxyl group, Y is a monovalent hydrocarbon group, R is an alkylene group having from 1 to 20 carbon atoms, Z is a group capable of reacting with a free radical, n is 0 or 1, a is 1, 2 or 3, b is 0, 1 or 2, c is 1, 2 or 3 and the sum of $a+b+c$ equals 4, and b) mixing said polyolefin, filler and organosilane under conditions which can provide free radicals in the mixture.

- 25 The inorganic filler must be combined with the coupler in such a fashion as to create an adherent bond between the inorganic filler and the coupler. The bonding can be accomplished either prior or subsequent to addition of the inorganic filler to the polymer. As previously mentioned, the bonding can be carried out in the presence or absence of a solvent for the coupler, in the presence or absence of the polymer matrix, and is preferably but not necessarily accomplished by heating the filler-coupler mixture at an elevated temperature up to 200° C or more.

- 30 The free radicals in the reaction mixture can be provided in a number of ways. Intensive mixing under conditions of high shear can cause rupture of the polyolefin molecules with resultant formation of free radicals. The necessary degree of shearing can be achieved by high speed mixing at elevated temperatures such as can be carried out by Henschel mixer or by lower speed mixing under compression such as mixing in a Banbury mixer. High speed mixing at 150 to 200° C and 200 to 1000 rpm for 3 to 10 minutes provides the necessary degree of shear as does lower speed mixing at 70 to 100 rpm under 5 to 100 pounds per square inch compression at the same temperature for the same time. An extrusion process can also provide the shearing effect required. As an example, polyolefin and inorganic filler can be added to a single screw extruder set at 150 to 210° C. The polyolefin and inorganic filler can be premixed or metered into the extruder in any desired ratio. For maximum dispersion, the extruder

screw should have a mixing section although good results can also be obtained with a standard PE extruder having an l/d of 18 to 1 or more. Other extrusion equipment which can be used herein include a twin-screw extruder such as manufactured by Welding Engineers, a continuous Banbury mixer such as manufactured by the Farrel Corporation and a KO—Kneader manufactured by Baker-Perkins. The filler-polyolefin composite can be extruded directly into finished products such as rods, films or pipes, or the extrudate can be chopped into pellets and used as a moulding compound which can be injection or compression moulded. As recognised by those skilled in the art, the above variables are interdependent and can be changed considerably and still perform the required task. Accordingly, they are set forth as suggested conditions and are in no way limitations upon the inventive process. Conditions set forth above can produce the degree of shearing necessary to provide compositions with the favourable combination of properties desired at even the lower levels of inorganic filler concentration. At higher concentrations of inorganic filler around 20 volume %, less severe conditions are required to produce the necessary amount of shearing. For instance, at 30% by volume inorganic filler, milling on rolls heated to 150 to 160° C for seven minutes or more will produce the desired combination of tensile and impact properties. As the inorganic filler content is increased to 40 volume % or more, the milling time can be reduced as low as 5 minutes. As a general rule, the higher the inorganic filler content, the less severe need be the mixing conditions to produce the shearing effect necessary.

The free radicals in the polymer-inorganic filler mixture can also be formed in other ways such as by the formation of the radicals on the surface of the inorganic filler. This can occur by oxidising some functional groups of the coupler to form peroxides or hydroperoxides or by attaching an organic peroxide or hydroperoxide to a coupler-treated inorganic surface in some other way. An example of one functional group which can be attached to an inorganic filler surface through a coupling agent and which can be oxidised to form a peroxide group adherently attached to the inorganic surface is the methacryloxy group. Upon heating the peroxy or hydroperoxy groups in the presence of the polyolefin, the groups will decompose to form free radicals which can then react with the olefinic polymer molecule. The only caution to be observed is that the amount of peroxide or hydroperoxide in the mixture, whether formed by oxidation of coupler groups or added separately to the mixture, is preferably kept at a level which will not result in the formation of more than about 1 cross-link per 10 polymer molecules in the matrix.

Following the mixing of polymer and inorganic filler in the presence of free radicals, the composite can be processed into an intermediate or final form using any of the techniques applicable to the processing of unmodified polyolefins. For instance, if the material were mixed under high shearing conditions, it could then be milled on heated rolls for one or more minutes and then compression moulded into sheets. Or the material could be extruded, chopped into pellets and injection moulded. Other processing techniques are also available.

The addition of antioxidant stabiliser is preferably carried out after the polyolefin and treated filler have been mixed together in the presence of free radicals. Mechanical properties of compositions having no stabiliser are identical with the properties of compositions having stabiliser added after thorough mixing of polymer and filler. If antioxidant is added to the polyolefin prior to compounding with the filler, the mechanical properties drop off substantially unless a significantly longer mixing time is employed or unless some other means are taken to render the antioxidant ineffective. Addition of peroxides or hydroperoxides can be used to inactivate the antioxidant. Regardless of how the antioxidant is rendered ineffective, it should be inactivated since, if present, it will react with the free radicals being formed in the polymer-filler mixture before the radicals can react with the functional groups on the coupler. As indicated above, the antioxidant can be inactivated by addition of oxidants such as peroxides and hydroperoxides or by heating and mixing the polymer and filler to cause the generation of free radicals in situ, or by some other means.

The extent of treatment necessary to inactivate the stabiliser depends upon the quantity and type of compound being used. One stabiliser, dilaurylthiodipropionate usually used at levels of about 500 parts per million, can be effectively overcome and the composite formed in the absence of antioxidant by simple milling at 150° C for five or six minutes. Other stabilisers, such as 2,6-di-tert-butyl-p-cresol which is often used at 50 to 1000 parts per million, requires 10 to 15 minutes milling to remove the stabiliser and prepare the composite. The milling time can of course be reduced by addition of peroxide to the mixture on the rolls.

Various other additives such as colourants, dyes and processing aids can also be used and added to the composite. Two or three parts of titanium dioxide per 100 parts of composite has been useful in whitening the finished material. A wide variety of dyes can also be employed. Small quantities of white mineral oil or stearic acid have also been of value as processing aids, particularly when the filler has an acicular nature with an 1/d

approaching 10 to 1 or when the filler is used at high levels of loading around 50 or 60%.

The invention is illustrated by the following Examples.

EXAMPLE 1

One thousand parts of finely divided anhydrous silica, having a maximum particle size of 5 microns and an average particle size of 1 micron, is treated with 16 parts of 3-trimethoxysilylpropyl methacrylate by adding the methacrylate coupler to the silica and mixing the two ingredients for 15 minutes at 50° C and 15 minutes at 110° C. The treated inorganic filler is then placed in a ball mill to break up any aggregate, after which time the inorganic filler is ready for further use.

Polyethylene having a density of 0.955 and the treated silica are combined in three different proportions to provide composites containing 20, 30 and 40% by volume inorganic filler. The preparation of the composite is achieved by adding the silica to the polyethylene on mill rolls heated to 170 to 180° C. Following addition of the silica, the two substances are milled together for 5 minutes. A duplicate set of compositions is prepared in exactly the same way except that a milling time of 15 minutes is used. Following removal from the mill rolls, the composite is compression moulded at 1000 pounds per square inch for 5 minutes, during which time the temperature is raised to 180° C over a 3 minute period and then lowered to or near to room temperature. Mechanical properties of the composites are reported in Table 1. Properties reported for Composite A correspond to the properties for the unmodified polyethylene used as the resinous component in Example 1.

EXAMPLE 2

Example 1 is repeated except that the quantity of coupler on the inorganic filler is reduced from 1.60% to 0.6% by weight. Properties are reported in Table 1.

EXAMPLE 3

One thousand parts of finely divided anhydrous silica having a maximum particle size of 10 microns and an average particle size of 2.1 microns is treated with 2 parts of 3-trimethoxysilylpropyl amine by adding the amine coupler dissolved in 1000 parts of methanol to the silica and mixing the slurry at room temperature for 15 minutes. After thorough mixing, the methanol is removed by heating the slurry at 110° C. The treated and dried inorganic filler is then placed in a ball mill to break up any aggregates, after which time the inorganic filler is ready for further use.

The composite is prepared as described in Example 1 using only a 15 minute milling time. Properties are reported in Table 1.

EXAMPLE 4

5 The procedure described in Example 3 is followed exactly except for this additional feature. To the mixture of inorganic filler and polymer on the mill rolls, oleic acid, equivalent to 2.1% of the inorganic filler in the mixture, is added to the mixture. The above procedure is carried out to provide a composite formulation containing 30% by volume inorganic filler. Properties are reported in Table 1.

EXAMPLE 5

15 The procedure set forth in Example 3 is followed exactly except that the inorganic filler is treated with .15% of vinyltriethoxysilane instead of 0.2% 3-triethoxysilylpropylamine. Properties are set forth in Table 1.

EXAMPLE 6

20 The procedure set forth in Example 1 is followed except that anhydrous silica having a maximum particle size of 10 microns and an average particle size of 2.1 microns is blended with a polymeric blend consisting of 9 parts polyethylene having a density of 0.955 and 25 1 part of an ethylene/vinyl acetate copolymer containing 50% polymerised ethylene. The inorganic filler and polymer are compounded to provide a composite formulation having 30% by volume inorganic filler. Properties are reported in Table 1. Properties

reported for Composite B in Table 1 belong to the unmodified polyblend.

EXAMPLE 7

The procedure set forth in Example 1 is followed except that anhydrous silica having a maximum particle size of 10 microns and an average particle size of 2.1 microns, pretreated with 0.2% 3-tri-methoxysilylpropyl methacrylate, is mixed with a polyblend consisting of 9 parts of polyethylene having a density of 0.96 and 1 part of an ethylene/ethylacrylate copolymer containing 50% polymerised ethylene. The mixture is milled for 15 minutes to provide a composite formulation having 30% by volume inorganic filler. Results are reported in Table 1. Properties reported for Composite C in Table 1 correspond to the mechanical properties for the polyblend set forth above unmodified by inorganic fillers.

EXAMPLE 8

Stereoregular polypropylene (Profax 6511) is milled for 15 minutes with an anhydrous silica described in Example 1 according to the procedure described in Example 1. ("Profax" is a registered Trade Mark). Results are reported in Table 1. Properties reported for Composition D belong to the polypropylene used above unmodified by the addition of inorganic filler material.

TABLE I

Composition	A	1			2			3		
Vol % filler	—	20	30	40	20	30	40	20	30	40
Impact strength	2.2	a) 5.5 b) 7.6	6.1 6.3	5.4 5.0	6.5 9.2	7.3 7.3	5.7 5.5	1.7	2.4	2.9
Yield strength	4100	a) 4400 b) 4400	4900 4900	5300 5100	4560 4420	4860 4850	5360 5250	4500	4900	5000
Tensile strength	2400	a) 2500 b) 2400	3200 3700	4300 4300	2770 2470	3400 3240	4240 4280	2900	4200	4500

a) 5 minute mill roll time
b) 15 minute mill roll time

Composition 1 demonstrates the effect of inorganic filler concentration and of milling time upon some of the preferred compositions of this invention. Comparison of Compositions 2 and 1 demonstrates the effect that coupler concentration has when 5 micron anhydrous silica is employed. Composition A indicates the properties possessed by the unmodified polyethylene which was used in Compositions 1 and 2. Compositions 3, 4 and 5 demonstrate the effect that different coupling agents have upon the properties of the finished composition. Examples 6, 7 and 8 demonstrate the practice of this invention with polymer matrices other than polyethylene.

EXAMPLE 9

The following series of polymeric compositions is presented to demonstrate the probability of existence of free radicals created by the milling of polymer and inorganic filler and the necessity of their occurrence in the presence of the coupler-treated inorganic filler.

- a) Polyethylene is milled on mill rolls heated to 150° C for 5 minutes, after which time it is compression moulded at 1000 pounds per square inch for 5 minutes at a maximum temperature of 180° C.
- b) Procedure (a) is followed except that anhydrous silica (maximum particle size 10 microns, average particle size 2.1 microns) is added to the polyethylene on the rolls and milled for 5 minutes to prepare a composite having 30% by volume inorganic filler.

- c) Procedure (b) is followed except that 0.1% by weight based on the polymer of 2,6-di-tert-butyl-p-cresol is added to the polyethylene before it is placed on the rolls. 40
- d) Procedure (b) is followed except that 0.25% by weight based on the inorganic filler of di-tert-butyl peroxide is added to the inorganic filler before it is placed on the rolls. 45
- e) Procedure (c) is followed except that 0.25% by weight based on the inorganic filler of di-tert-butyl peroxide is added to the inorganic filler before it is placed on the rolls. 50
- f) Procedure (b) is followed except that the inorganic filler is pretreated with 0.2% by weight based on the inorganic of 3-trimethoxysilylpropyl methacrylate before the inorganic filler is added to the polymer. 55
- g) Procedure (f) is followed except that 0.1% by weight based on the polymer of 2,6-di-tert-butyl-p-cresol is added to the polyethylene before it is placed on the rolls. 60
- h) Procedure (f) is followed except that 0.25% by weight based on the inorganic filler of di-tert-butyl peroxide is added to the inorganic filler after the coupler is added and before the inorganic filler is added to the polymer. 65
- i) Procedure (h) is followed except that 0.1% by weight based on the polymer of 2,6-di-tert-butyl-p-cresol is added to the polymer before milling. 70

4	5	B	6	C	7	D	8						
30	20	30	40	—	30	—	20	30	40	—	20	30	40
2.8	2.9	3.6	3.3	1.8	2.2	1.2	1.6	1.7	1.8	0.5	0.7	0.7	0.6
5000	2200	4670	5070	3830	4400	3970	4400	4500	4900	3600	4150	3890	3680
4400	2350	3660	4540	1940	3400	1870	3000	3800	4400	3100	3660	3550	3540

- j) Procedure (f) is followed except that 0.2% by weight based on the inorganic filler of ethyl (β -triethoxysilyl) propionate is adherently bonded to the inorganic filler instead of 3-trimethoxysilylpropyl methacrylate. Ethyl (β -triethoxysilyl) propionate is an organosilane which, when bonded to an inorganic filler contains no functional groups which can react with a free radical.
- Results of mechanical testing of the above compositions are reported in Table II below and are plotted in graphical form in the Drawing to demonstrate the surprising advantage of conducting the mixing in such fashion as to generate free radicals in the presence of a coupling agent which can react with free radicals. The 2,6-di-tert-butyl-p-cresol used in Compositions 9(c), (e), (g), and (i) is an antioxidant which serves to react with free radicals immediately upon their formation and to remove them from the mixture. Hence, free radicals cannot be present in the preparation of Compositions 9(c), (e), (g), or (i) using the 5 minute milling time specified. Inspection of the above-described procedures and the Figure will indicate that free radicals are present in the preparation of three compositions employing an organosilane coupler, Compositions 9(f), (h) and (j). The coupler used in Composition (j) is not actually a coupler, however, since it is not capable of reaction with a free radical. Only in Compositions (f) and (h) is there present a free radical-reactive coupler together with free radicals. The outstanding improvements in mechanical properties manifested by Compositions 9(f) and (h) form the basis for this invention.

TABLE II

Composition 9	a	b	c	d	e	f	g	h	i	j
Impact strength ft.lbs./in. of notch	2.2	0.4	0.3	0.3	0.4	3.4	0.3	3.8	0.5	0.3
Yield strength, psi	4100	no yield	2900	4050	3200	5000	3700	5000	3750	3500
Tensile strength, psi	2400	3600	2600	4000	2900	3900	3500	4000	3600	3400

EXAMPLE 10

The present Example is provided to demonstrate the generation of free radicals and its consequent effect upon mechanical properties by mixing means other than simple mill rolling.

Polyethylene having a density of 0.955 and anhydrous silica (maximum particle size 10 microns, average size 2.1 microns) are added to a Banbury mixer and mixed for 5 minutes at 170° C and 78 rpm. The pressure on the ram is 20 pounds. After Banbury mixing, the composite is mill rolled for 1 minute at 150° C, after which time the composite is compression moulded at 1000 pounds per square inch for 5 minutes using a maximum moulding temperature of 180° C. The above procedure is carried out to provide compositions containing 20, 30 and 40 volume % inorganic filler. Results are reported in Table III below.

The above procedure is repeated except that the silica is pretreated with 0.4% based on the weight of the silica of 3-trimethoxysilylpropyl methacrylate. Results are reported in Table III below.

EXAMPLE 11

The procedure in Example 10 is followed except that in place of the 5 minutes of Banbury mixing followed by 1 minute of mill rolling is substituted 3 minutes of mill rolling. Results are reported in Table III below. As can be seen from the data, three minutes of milling does not provide sufficient free radicals to cause an enhancement of mechanical properties.

Comparison of Compositions 10a and 11a indicates that the generation of free radicals achieved in Composition 10a has little effect upon the mechanical properties of the finished composition in the absence of a coupling agent. Examination of Composition 11b indicates that the use of a coupling agent in conjunction with mixing conditions which are not likely to produce large amounts of free radicals produces compositions very similar in properties to those using no coupling agent. Comparison of Compositions 10b and 11b indicates that the use of a coupler, in combination with conditions likely to generate free radicals, produces finished polymeric compositions having the required excellent combination of properties.

TABLE III

Composition	10a			10b			11a			11b		
Filler, volume %	20	30	40	20	30	40	20	30	40	20	30	40
Impact strength, ft.lbs./in.notch	0.7	0.3	0.3	2.9	3.4	3.0	0.3	0.3	0.4	0.6	1.5	3.1
Yield strength, psi	4500	4200	4500	4600	4800	5100	4500	4700	5100	4400	4800	5100
Tensile strength, psi	3200	4000	4400	2600	3500	4400	3700	4400	4900	2700	3600	4400

EXAMPLE 12

One thousand parts of feldspar, which passes through a 325 mesh sieve of the U.S. Sieve Series and has an average particle size of 30 microns, is treated with 20 parts of 3-trimethoxysilylpropyl methacrylate as described in Example 1.

A polyethylene copolymer containing 5% polymerised propylene is mixed with the feldspar on mill rolls heated to 185° C for 10 minutes. The polymer and feldspar are mixed in quantities which provide a composite containing 40% by volume inorganic filler. The mixture is compression moulded as described in Example 1. The finished composition has an impact strength 25% higher and a tensile strength and a yield strength 15% higher than the unfilled polymer.

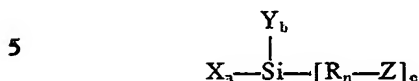
Uses for the modified polyolefins of this

invention are generally those where the unmodified polyolefins find application but where additional tensile strength, rigidity and impact strength can be tolerated or are desired. Examples of specific articles which can be manufactured from the compositions described herein include wire coatings, plastic packages, pipes, air conditioner ducts, heater outlets, moulded housings, housewares and toys. Preferably, those manufacturing techniques are used which will provide manufactured articles having the same desirable combination of mechanical properties as are possessed by the compositions described herein.

WHAT WE CLAIM IS:—

1. A polymeric composition comprising a polyolefin as hereinbefore defined, from 10 to 60% by volume based on the total com-

position of an inorganic filler having an average surface area of from 0.5 to 10 square meters per gram and an l/d ratio of 10 to 1 or less, and an organosilane of the formula



where X is a hydrolysable group capable of reacting with a hydroxyl group, Y is a monovalent hydrocarbon group, R is an alkylene group having from 1 to 20 carbon atoms, Z is a group capable of reacting with a free radical, n is 0 or 1, a is 1, 2 or 3, b is 0, 1 or 2, c is 1, 2 or 3 and the sum of $a+b+c$ equals 4.

2. A polymeric composition according to Claim 1, said composition being characterised by an Izod notched impact strength at least 10% greater than the impact strength of the unfilled polyolefin and by a yield strength and tensile strength at least undiminished by comparison to the corresponding strengths of the unfilled polyolefin.

3. A polymeric composition according to either of Claims 1 and 2 wherein said polyolefin is polyethylene having a density of at least 0.92 grams per cubic centimetre.

4. A polymeric composition according to either of Claims 1 and 2 wherein said polyolefin is isotactic polypropylene.

5. A polymeric composition according to either of Claims 1 and 2 wherein said polyolefin is an olefinic copolymer containing at least 50% by weight polymerised olefin.

6. A polymeric composition according to either of Claims 1 and 2 wherein said polyolefin is a polyblend containing at least 50% by weight polymerised olefin.

7. A polymeric composition according to any of Claims 1 to 6 wherein said inorganic filler is present in a quantity ranging from 20 to 40% by volume of the total composition.

8. A polymeric composition according to any of claims 1 to 7 wherein said inorganic filler is a finely divided anhydrous silica having a maximum particle size of 10 microns.

9. A polymeric composition according to any of Claims 1 to 8 wherein said organosilane of the formula



is limited as follows:

X is an alkoxy or chloro group, Z is a group containing ethylenic unsaturation, R is an alkylene group containing from 3 to 18 carbon atoms, a is 3, b is 0, c is 1 and n is 1.

10. A polymeric composition according to

Claim 9 wherein said organosilane is 3-trimethoxysilylpropyl methacrylate.

11. A polymeric composition according to any of Claims 1 to 10 wherein said composition is characterised by an Izod notched impact strength at least 20% greater than the unfilled polyolefin.

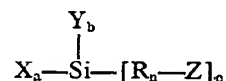
12. A polymeric composition according to any of Claims 1 to 11 wherein said composition is characterised by an Izod notched impact strength, yield strength and tensile strength which are each at least 10% greater than the corresponding properties of the unfilled polyolefin.

13. A polymeric composition according to any of Claims 1 to 12 wherein the Izod notched impact strength is at least double the impact strength of the unfilled polyolefin.

14. A polymeric composition according to Claim 1 substantially as described in any of the Examples.

15. A process for preparing a polymeric composition comprising

- a) combining a polyolefin as hereinbefore defined and from 10 to 60% by volume based on the total composition of an inorganic filler having an average surface area of from 0.5 to 10 square meters per gram and an l/d ratio of 10 to 1 or less, said filler having adherently bonded to its surface an organosilane of the formula



where X is a hydrolysable group capable of reacting with an hydroxyl group, Y is a monovalent hydrocarbon group, R is an alkylene group having from 1 to 20 carbon atoms, Z is a group capable of reacting with a free radical, n is 0 or 1, a is 1, 2 or 3, b is 0, 1 or 2, c is 1, 2 or 3 and the sum of $a+b+c$ equals 4, and

- b) mixing said polyolefin and said filler under conditions which can provide free radicals in the mixture.

16. A process according to Claim 15 in which there is produced a polymeric composition according to Claim 2.

17. A process according to Claim 15 in which there is produced a polymeric composition according to any of Claims 3 to 14.

18. A process according to Claim 15 wherein the adherent bond between said filler and organosilane is achieved by blending the two ingredients in the absence of any solvent and heating the mixture at an elevated temperature up to 200° C.

19. A process according to any of Claims 15 to 18 wherein said conditions which can

provide free radicals in the mixture consist of mixing said polyolefin and said filler under conditions of high shearing.

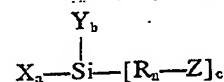
20. A process according to Claim 19 wherein said mixing to produce high shearing is carried out on a mill roll.

21. A process according to Claim 19 wherein said mixing to produce high shearing is carried out in a Banbury mixer.

10 22. A process according to any of Claims 15 to 21 wherein said mixing of polyolefin and filler is carried out in the absence of a stabiliser for polyolefins.

15 23. A process according to Claim 15 substantially as described in any of the Examples.

20 24. An article of manufacture comprising a polyolefin as hereinbefore defined, from 10 to 60% by volume based on the total composition of an inorganic filler having an average surface area of from 0.5 to 10 square meters per gram and an l/d ratio of 10 to 1 or less, and an organosilane of the formula



25 where X is a hydrolysable group capable of reacting with an hydroxyl group, Y is a monovalent hydrocarbon group, R is an alkylene group having from 1 to 20 carbon atoms, Z is a group capable of reacting with a free radical, n is 0 or 1, a is 1, 2 or 3, b is 0, 1 or 2, c is 1, 2 or 3 and the sum of $a+b+c$ equals 4, said article being characterised by an Izod notched impact strength at least 10% greater than the impact strength of the unfilled article and by a yield strength and tensile strength at least undiminished by comparison to the corresponding strength of the unfilled article. 30 35

25. A polymeric composition produced by a process according to any of Claims 15 to 23. 40

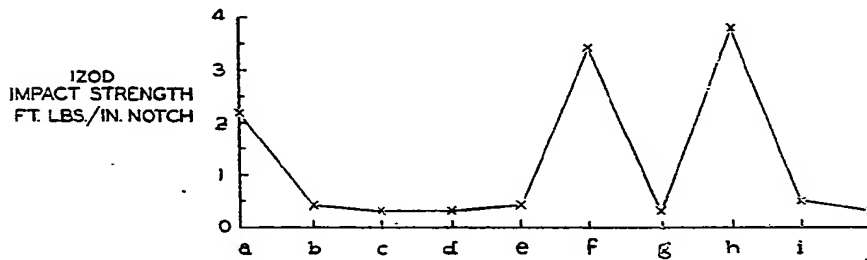
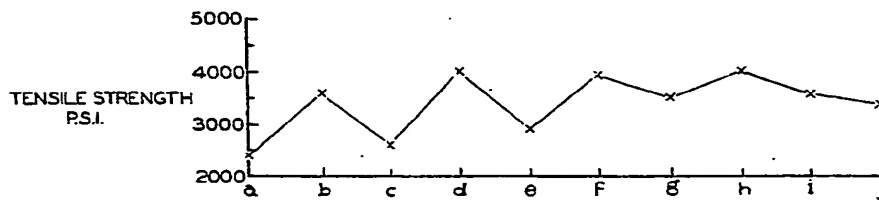
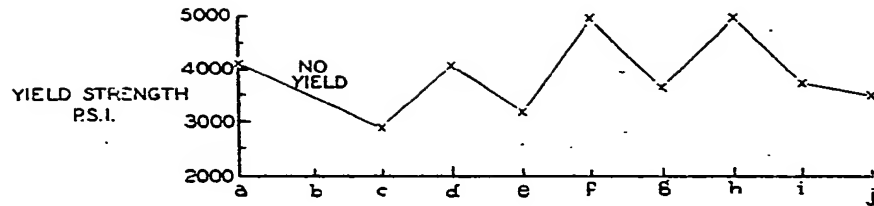
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COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*

LEGEND:

- a. POLYETHYLENE UNFILLED
- b. POLYETHYLENE FILLER
- c. POLYETHYLENE, FILLER, ANTIOXIDANT
- d. POLYETHYLENE, FILLER, PEROXIDE
- e. POLYETHYLENE, FILLER, PEROXIDE, ANTIOXIDANT
- f. POLYETHYLENE, FILLER, COUPLER
- g. POLYETHYLENE, FILLER, COUPLER, ANTIOXIDANT
- h. POLYETHYLENE, FILLER, COUPLER, PEROXIDE
- i. POLYETHYLENE, FILLER, COUPLER, PEROXIDE, ANTIOXIDANT
- j. POLYETHYLENE, FILLER, NON-REACTIVE COUPLER

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